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DFT study on nonlinear optical properties of lithium-doped corannulene

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The effects of lithium doping on the nonlinear optical properties of new electrodes (lithium-doped corannulene) were investigated in detail. Nine dynamically stable geometries of Li_n-$C_{20}H_{10}$ (n=1, 2) are predicted by B3LYP/6-31G(d,p). Among these nine structures, the largest first static hyperpolarizability (β_0) is computed to be 15314 au, which is dramatically larger than the β_0 value of 74 au for $C_{20}H_{10}$, indicating that Li doping plays an important role in elevating the first hyperpolarizability of corannulene.

corannulene ($C_{20}H_{10}$), lithium doped, nonlinear optical properties, first hyperpolarizability, DFT

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The extensive number of works that have been performed over the past two decades to investigate the nonlinear optical (NLO) properties of novel NLO materials [1–7] have been devoted to discovering the important/key influencing factors that can lead to dramatic increases in the first hyperpolarizability [8]. The strategies used mainly focused on utilizing molecules that contain extended π-electron systems [9] or that can be characterized as planar donor-π-conjugated bridge-acceptor (D-π-A) types [10,11] or that contain a twisted π-electron system [12]. Incorporation of alkali metals into the organic compounds provides an alternative, efficient approach to elevate the first hyperpolarizability [13–18]. A number of fascinating NLO materials with Li-doped complexes have recently been reported [19–26]. These Li-doped complexes have shown a significantly large NLO response, and the valence electrons of the Li atoms play a crucial role in elevating the NLO value of these compounds. Based on these reports, we chose corannulene as a model with which to design novel Li-doped NLO materials with a desirably large NLO value.

The first reported synthesis of corannulene ($C_{20}H_{10}$) was published by Barth and Lawton [27] in 1966, with this molecule showing aromatic character [28] and stability at high temperatures [29]. Corannulene can be thought of as the upper third of a C_{60} molecule with the valences of the outermost atoms saturated by H atoms. The molecule resembles a shallow bowl with C_{5v} symmetry (Figure 1) and the six-membered rings at the periphery lie significantly out of the plane. $C_{20}H_{10}$ exhibits a number of interesting properties [30,31] and its complexes with ions or atoms, such as alkaline cations or transition metal atoms [32–35], have been studied both experimentally and theoretically. Following the discussion above, we investigated corannulene molecules with Li doping for the design of novel NLO materials.

In the current work, to investigate the effect of Li doping on the NLO properties of corannulene, we predict the structural and electronic properties of Li_n-$C_{20}H_{10}$ (n=1, 2) at the atomic level. It is found that the large hyperpolarizabilities of Li_n-$C_{20}H_{10}$ (n=1, 2) strongly depend upon the concentration and position of the Li atoms.

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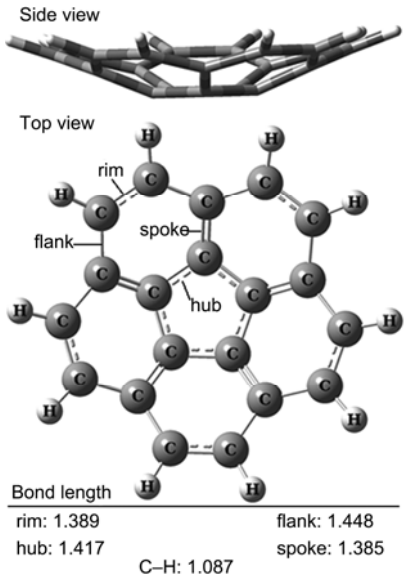

Figure 1 Optimized structure of corannulene (C_{5v} symmetry). There are four types of C–C bonds: hub, spoke, flank, and rim (bond lengths in Å).

1 Theoretical method and computational details

All calculations were performed using the Gaussian 03 [36] package and all structures were optimized using Becke's three-parameter hybrid functional combined with the Lee, Yang, and Parr (LYP) correlation functional (B3LYP). The calculated Hessian matrices show that all optimized geometries are local minima with no imaginary frequencies, thus indicating they are all dynamically stable. The first hyperpolarizabilities were evaluated using the finite field approach at the B3LYP level. The 6-31G(d,p) basis set was employed for all calculations. The total energy of a molecular system in the presence of a homogeneous electric field can be expressed as

$$E = E^{(0)} - \mu_1 F_1 - \frac{1}{2}\alpha_{ij}F_iF_j - \frac{1}{6}\beta_{ijk}F_iF_jF_k - \frac{1}{24}\gamma_{ijkl}F_iF_jF_kF_l - \ldots, \quad (1)$$

where $E^{(0)}$ is the energy of the molecule in the absence of an electronic field, μ is the component of the dipole moment vector, α is the linear polarizability tensor, and β and γ are the first and second hyperpolarizability tensors, respectively. For a molecule, the average dipole moment (μ_0) and polarizability (α_0) are defined as follows:

$$\mu_0 = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}, \quad (2)$$

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right). \quad (3)$$

The first hyperpolarizability is defined as

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}, \quad (4)$$

where

$$\beta_i = \frac{3}{5}\left(\beta_{iii} + \beta_{ijj} + \beta_{ikk}\right), \ i, j, k = x, y, z. \quad (5)$$

2 Results and discussion

2.1 Equilibrium geometries

The bowl-shaped structure of corannulene ($C_{20}H_{10}$) is well known, and we have adopted similar structural parameters to those reported in previous theoretical and experimental work [37]. The optimized structures and corresponding geometrical parameters of corannulene are shown in Figure 1. Corannulene's unique bowl shape offers a variety of binding possibilities for lithium atoms, including binding to either the concave or convex surfaces of the molecule. In this step, various configurations of Li doping were considered. Figure 2 shows the optimized structures of Li_n-$C_{20}H_{10}$ (n=1, 2). The corresponding distances between Li and C atoms (labeled C1 to C6 in Figure 2) are listed in Table 1. The given geometries of Li_n-$C_{20}H_{10}$ (n=1, 2) are all in C_1 symmetry.

For doped structures with one Li, two different structures (**1a** and **1b**, Figure 2) are obtained. The binding energy and NBO charge on the Li atom are listed in Table 1. The calculations show that the Li atom can bind to the convex or concave side of the six-membered ring, as shown in **1a** and **1b**, respectively. The C–Li distances listed in Table 1 indicate that the location of the Li atom is close to the center of a six-membered ring. The binding energies of **1a** and **1b** are –69.7 and –74.1 kJ/mol, respectively, which is in good agreement with the results of Zhang et al. [31]. The NBO charges on the Li atoms of **1a** and **1b** are 0.918 (e) and 0.942 (e), respectively, indicating charge transfer from Li to corannulene.

Turning our attention to the doped geometries with two Li atoms, it can be seen that the two Li atoms can be located either at the concave or at the convex side. From a search of the possible isomers that such a system might adopt, we present seven different structures (**2a–2g** in Figure 2) of Li_2-$C_{20}H_{10}$ with the two Li atoms located on the same side (either convex or concave) or at opposite sides of corannulene. Table 1 lists the computed binding energies and average NBO charges on the Li atoms. The structures **2a** and **2b** have two Li atoms sitting on the convex side of the corannulene molecule. The binding energies of these structures are –162.0 and –163.8 kJ/mol for **2a** and **2b**, respectively. **2c** and **2d** have two Li atoms locating on the concave side of the corannulene molecule. The binding energies of **2c** and **2d** are –139.3 and –152.2 kJ/mol, respectively, both of which are higher in energy than **2a** or **2b** (on the convex side). The structures **2e**, **2f**, and **2g** have the two Li atoms adsorbed on the two opposing sides of the corannulene. The binding energies for these structures are –169.4 (**2e**), –178.2

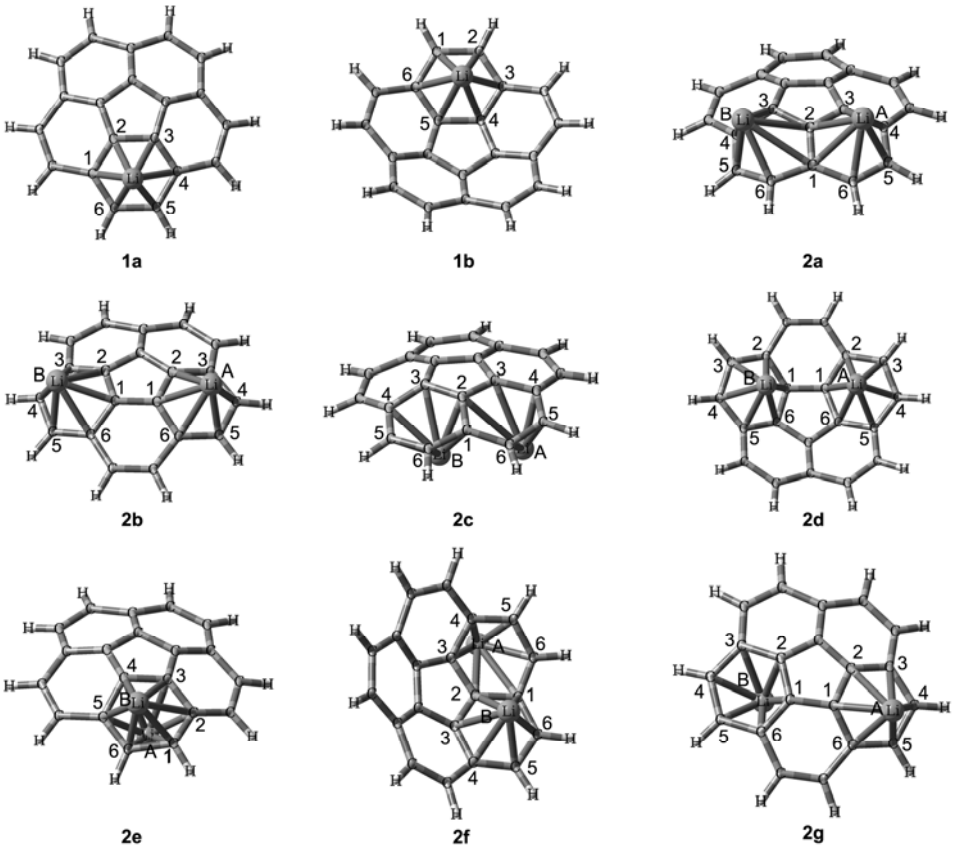

Figure 2 Optimized geometries of Li_n-$C_{20}H_{10}$ (n=1, 2).

Table 1 Selected optimized geometrical parameters (Å), NBO charges on Li atoms, and binding energies (E_b, kJ/mol) for Li_n-$C_{20}H_{10}$ (n=1, 2) complexes[a)]

	C1–Li	C2–Li	C3–Li	C4–Li	C5–Li	C6–Li	q(Li)[b)]	E_b (kJ/mol)[c)]
1a	2.288	2.211	2.315	2.434	2.158	2.140	0.918	–69.7
1b	2.178	2.185	2.221	2.253	2.244	2.206	0.942	–74.1
2a	2.370	2.279	2.229	2.267	2.121	2.163	0.851	–162.0
	2.802	2.650	2.211	2.138	2.081	2.201		
2b	2.204	2.442	2.519	2.143	2.110	2.220	0.882	–163.8
	2.204	2.443	2.520	2.143	2.110	2.220		
2c	2.969	3.004	2.516	2.129	2.076	2.349	0.608	–139.3
	2.185	2.296	2.401	2.333	2.247	2.217		
2d	2.572	2.444	2.240	2.156	2.173	2.337	0.643	–152.2
	2.573	2.444	2.240	2.156	2.174	2.338		
2e	2.150	2.789	2.667	2.216	2.179	2.114	0.862	–169.4
	2.377	2.132	2.191	2.456	2.246	2.162		
2f	2.744	2.593	2.199	2.170	2.105	2.180	0.881	–178.2
	2.350	2.332	2.201	2.162	2.142	2.177		
2g	2.185	2.514	2.655	2.181	2.113	2.178	0.897	–172.5
	2.319	2.204	2.181	2.165	2.171	2.251		

a) The data for Li_2-$C_{20}H_{10}$ consist of two types (from structure **2a** to **2g**). The first row for each structure refers to the "A" type Li atom and the second row refers to the "B" type Li atom (see Figure 2). b) The NBO charges of two Li-doped systems are reported as average values. c) E_b=E(Li_n-$C_{20}H_{10}$)−[nE(Li)+E($C_{20}H_{10}$)] (n=1, 2).

Table 2 Static first hyperpolarizability (β_0), transition energies (ΔE), and oscillating strengths (f_0) for $C_{20}H_{10}$ and Li_n-$C_{20}H_{10}$ (n=1, 2) calculated using B3LYP/6-31G(d,p)

Property	$C_{20}H_{10}$	**1a**	**1b**	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**
β_x (au)	–74	–3145	–10	–6742	121	–1517	16	–7521	–5391	8346
β_y (au)	–4	–1151	194	–6394	–6320	–1879	–240	881	–1070	986
β_z (au)	1	3076	462	12173	13340	5244	6149	2131	3458	4936
β_0 (au)	74	4547	501	15314	14762	5773	6154	7866	6434	9746
f_0	0.099	0.059	0.074	0.029	0.039	0.036	0.039	0.016	0.077	0.041
ΔE (eV)	6.366	2.190	5.205	0.947	1.228	2.090	2.048	1.547	1.635	1.409

(**2f**), and −172.5 kJ/mol (**2g**), meaning that they are more stable than those geometries with the two Li atoms lying on the same side. This therefore suggests that repulsion between the two Li atoms may play an important role in determining the stability of Li-doped corannulene. Interestingly, from the computed binding energies (see Table 1), one can see that adding a second Li atom to the one-Li-doped structures is thermodynamically favorable.

2.2 Static first hyperpolarizabilities

The calculated electronic properties of Li_n-$C_{20}H_{10}$ (n=0, 1, 2) are given in Table 2. One can see that the static first hyperpolarizabilities (β_0) values of $C_{20}H_{10}$ are only 74 au. For the one-doped systems, the β_0 value of Li-$C_{20}H_{10}$ is 4547 au (**1a**) and 501 au **(1b)**, respectively. In other words, the β_0 value of **1a** is almost 10 times larger than that of **1b**, indicating that a dramatic effect on the first hyperpolarizability results from a variation in the Li atom location. For the two-Li-doped systems, the value of β_0 decreases in the order 15314 (**2a**)>14762 (**2b**)>9746 (**2g**)>7866 (**2e**)>6434 (**2f**)> 6154 (**2d**)>5244 (**2c**) au. It is also interesting to compare the β_0 value of Li_2-$C_{20}H_{10}$ with other known systems that possess large β_0 values. The range of β_0 values of Li_n-$C_{20}H_{10}$ (n=1, 2) is from 5244 to 15314 au, which is close to that of the Li@calix[4]pyrrole [8] (3385–15682 au). Comparison among our results shows that the β_0 values of two-Li-doped systems are larger than those of the one-Li-doped systems. From Table 2 and Figure 2, we propose that the β_0 value of Li_n-$C_{20}H_{10}$(n=1, 2) systems is strongly associated with the concentration and location of the Li.

It is well known that the β_0 value of a Li atom itself is close to zero; therefore, it begs the question of how does it cause the large β_0 value on Li_n-$C_{20}H_{10}$ (n=1, 2)? According to a two-level expression [38], the β_0 value is dependent on three factors: the excitation energy (ΔE), the oscillator strength (f_0), and the difference in dipole moment ($\Delta\mu$) between the crucial transition states. In the two-level expression, the third power of the transition energy is inversely proportional to the β_0 value. Therefore, for the Li_n-$C_{20}H_{10}$ (n=1, 2) systems, the low transition energy is the decisive factor in providing the large β_0 value. In this work, TD-DFT calculations were carried out to obtain the crucial excited states of the Li_n-$C_{20}H_{10}$ (n=1, 2) systems, with the results listed in Table 2. The ordering of the ΔE values is 0.947 (**2a**)<1.228 (**2b**)<1.409 (**2g**)<1.547 (**2e**)<1.635 (**2f**)<2.048 (**2d**)<2.090 (**2c**)<2.190 (**1a**)<5.205 (**1b**)<6.366 ($C_{20}H_{10}$) eV. One finds that the variation in transition energy of Li_n-$C_{20}H_{10}$ (n=0, 1, 2) is related to the corresponding structures. In addition, Table 3 lists the nature of these crucial transitions. Taking **1a** and **1b** as illustrative examples, owing to the different manners of transition between **1a** (HOMO→LUMO+2) and **1b** (HOMO→LUMO+9), one can find the difference in the β_0 value for these two structures.

3 Conclusions

In the present work, we theoretically designed novel organic electrode compounds Li_n-$C_{20}H_{10}$ (n=1, 2). The computed NBO charges show that the Li atom is ionized and transfers electrons to corannulene. The β_0 values of Li_n-$C_{20}H_{10}$ (n=1, 2) are predicted to be significantly large, about 10–200 times greater than for $C_{20}H_{10}$. We suggest that β_0 values of Li_n-$C_{20}H_{10}$ (n=1, 2) systems are strongly dependent on the concentration and location of the Li. As a result, our investigation may direct attention to the design of new electrodes with large NLO responses via the use of lithium metal doping.

Table 3 Nature of transition in Li_n-$C_{20}H_{10}$ (n=1, 2)

	Transition	C_i[a)]
1a	HOMO→LUMO+2	0.76
1b	HOMO→LUMO+9	0.74
2a	HOMO→LUMO	0.65
2b	HOMO→LUMO+2	0.68
2c	HOMO→LUMO+2	0.67
2d	HOMO→LUMO+3	0.61
2e	HOMO→LUMO+1	0.67
2f	HOMO→LUMO+2	0.66
2g	HOMO→LUMO+2	0.66

a) Configuration interaction coefficient.

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